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OUTGASSING

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ABSTRACT

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Outgassing rate data based on the investigations of other authors and our own measurements are reviewed. It is shown that outgassing rates depend on the material, its treatment, and on the special conditions of application. In order to be able to establish the most favorable conditions for the evacuation of ultrahigh-vacuum apparatus, the fundamental physical processes (physical sorption, chemisorption, diffusion, solubility, etc.) that determine the outgassing process must be known. In conjunction with the corresponding physical laws, the above-mentioned outgassing data permit conclusions concerning the lowest pressures now attainable in ultrahigh-vacuum systems.

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AUTHOR

The achievement of the low pressures characteristic of the ultrahigh-vacuum region depends decisively on the question of the outgassing of the materials forming the vessel walls and the elements of the vacuum chamber. Empirical measurements of the outgassing rates of different materials (measured in $\text{torr} \cdot \text{l} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2}$) have been made by numerous authors [1-5, 7-10, 14, 15]. The majority of these measurements relate to the evolution of gas from specimen materials immediately after their introduction into the vacuum and, indeed, at room temperature, without the materials having been subjected to any preliminary treatment. In most cases the methods used to measure the outgassing rate have been very similar (see Fig. 1). The gas is pumped out of the measuring chamber containing the specimen across a resistance and the flow calculated from the resulting pressure drop. Fig. 2 presents a review of gas evolution measurements based on the data of various authors*. Detailed discussions of the numerical

*Pressure in the measuring chamber as a function of time for a known rate of evacuation.



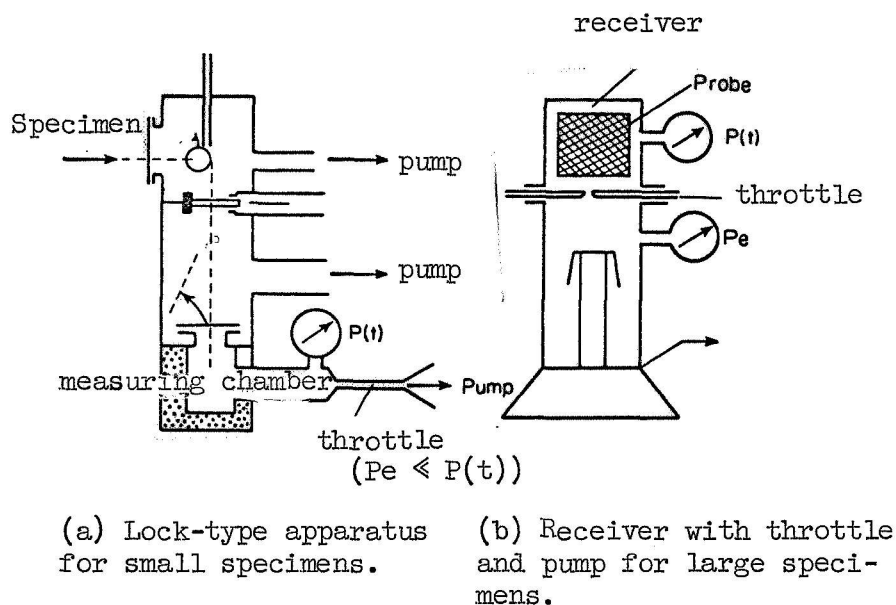


Fig. 1. Apparatus for measuring gas evolution.

values will be found in [1, 3, 8, 15, 16]. Particularly important are those cases in which the author not only measured the total pressure of the gases evolved, but made a partial pressure analysis of the gas mixtures present. At the same time, the results of such partial pressure analyses must be treated with considerable caution, since significant changes in the partial pressure composition may occur due to exchange with the vessel walls, and this will falsify the analysis. Dayton [3] has a particularly detailed and critical discussion of the considerations relating to outgassing data obtained in this way. For the partial pressure p_n of the n -th component of the gas mixture he ar-

rives at the following formula:

$$p_n = \frac{\sum_m q_{n,m} F_m - V(dp_n/dt)}{\sum_m f_{n,m} e_{n,m} F_m + S_n}$$

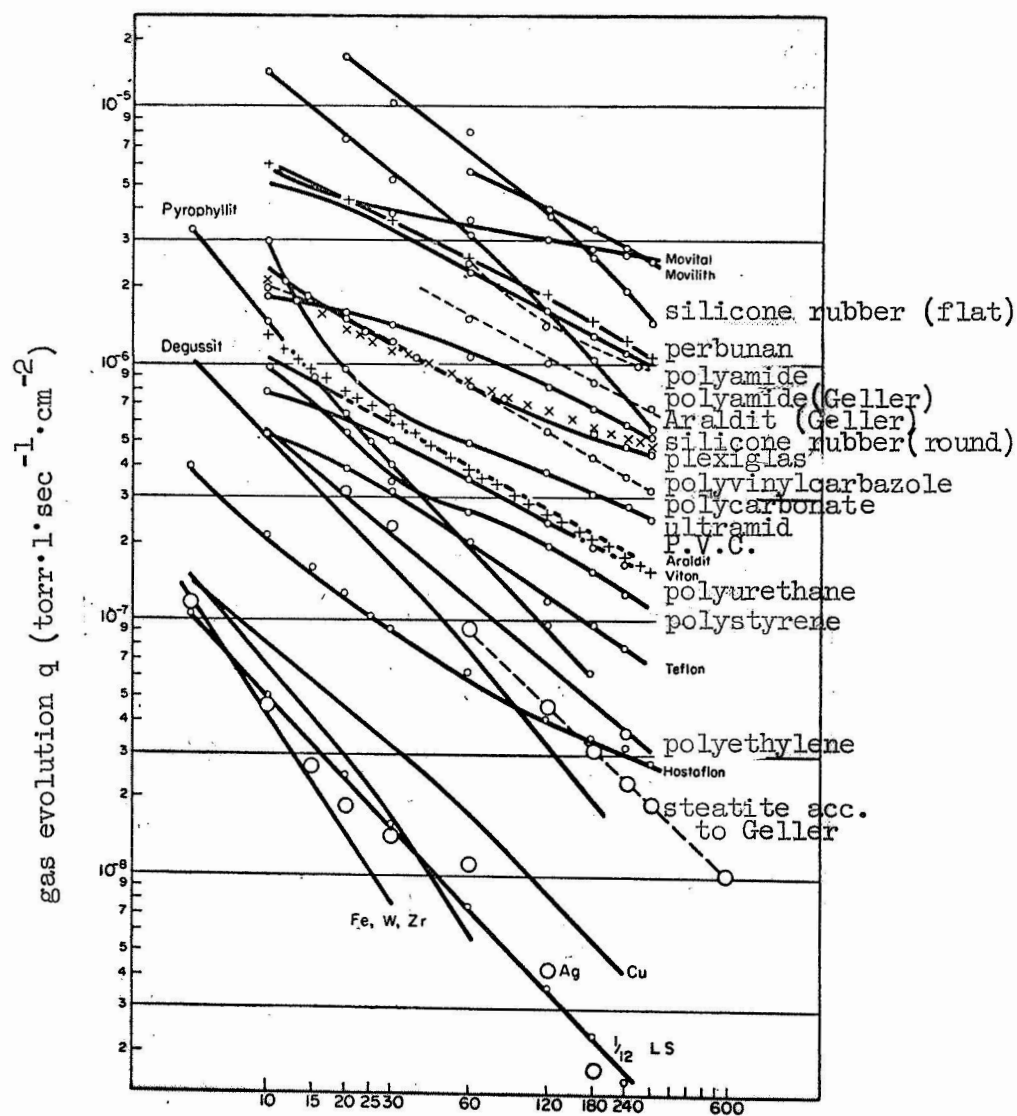


Fig. 2. Gas evolution q as a function of time for different materials (based on measurements of various authors).

where q = gas evolved ($\text{torr} \cdot \text{l} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2}$), F = surface area (cm^2), f = effusion factor, e = adsorption coefficient, S = rate of evacuation for the n -th component of the gas. The application of this formula presupposes a knowledge of the elementary constants as functions of the surface fraction (subscript m) and the nature of the gas (subscript n).

Various authors have concerned themselves with the investigation

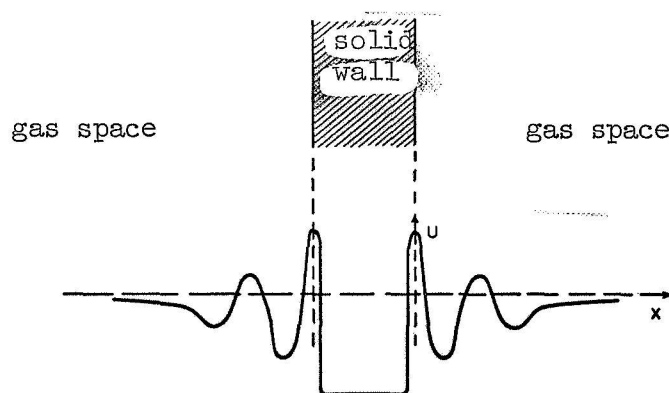


Fig. 3. Variation in potential U (schematic) for a neutral molecule approaching and passing through a solid wall.

of the elementary processes involved in outgassing. Let us consider (Fig. 3) the different potential values (U) that determine the forces between a solid wall and a free molecule as it approaches the wall or passes through it. The gas molecule that approaches a solid wall first enters a quite shallow potential well without exceeding a potential threshold and hence is only quite loosely bound (physical adsorption). After exceeding a low potential threshold, it then enters a more tightly bound state at the surface of the solid wall (chemisorption). From this state, having exceeded a further potential threshold, a gas molecule can go over into the dissolved state inside the solid. On re-emerging on the opposite side of the wall, it undergoes desorption, passing through the phases described in connection with adsorption in the opposite order. If the gas particles concerned are not atoms, but molecules, the step of dissociation into atoms may intervene between chemisorption and dissolution in the solid, while an

analogous recombination step may be added on the desorption side.

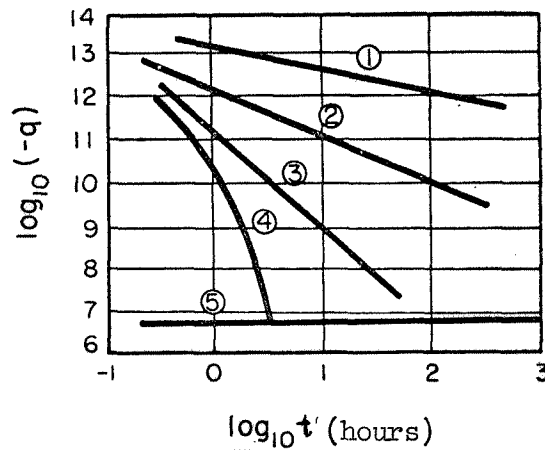


Fig. 4. Gas evolution q as a function of time t (schematic after Schram).

- (1) $q \sim \frac{1}{\sqrt{t}}$ diffusion
- (2) $q \sim \frac{1}{t}$ without adsorption $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$ with or without dissociation with adsorption $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$ with dissociation without dissociation when p is small
- (3) $q \sim \frac{1}{t^2}$ without adsorption with dissociation $E = E_0$
 $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$
- (4) $q \sim e^{-at}$ without adsorption without dissociation $E = E_0$
 $E = E_0 - \alpha \frac{n}{n_s}$ and $\frac{1}{n} \ll \beta$ with adsorption without dissociation
 $E = E_0$
- (5) $q = q_0$ permeation in stationary region.

Gas evolution:

comparison of pressure-time curves of specimens of the same material but different thickness.

Thickness of R 30 d = 4 mm }
 R 30 ü = 1.6 mm } silicone rubber

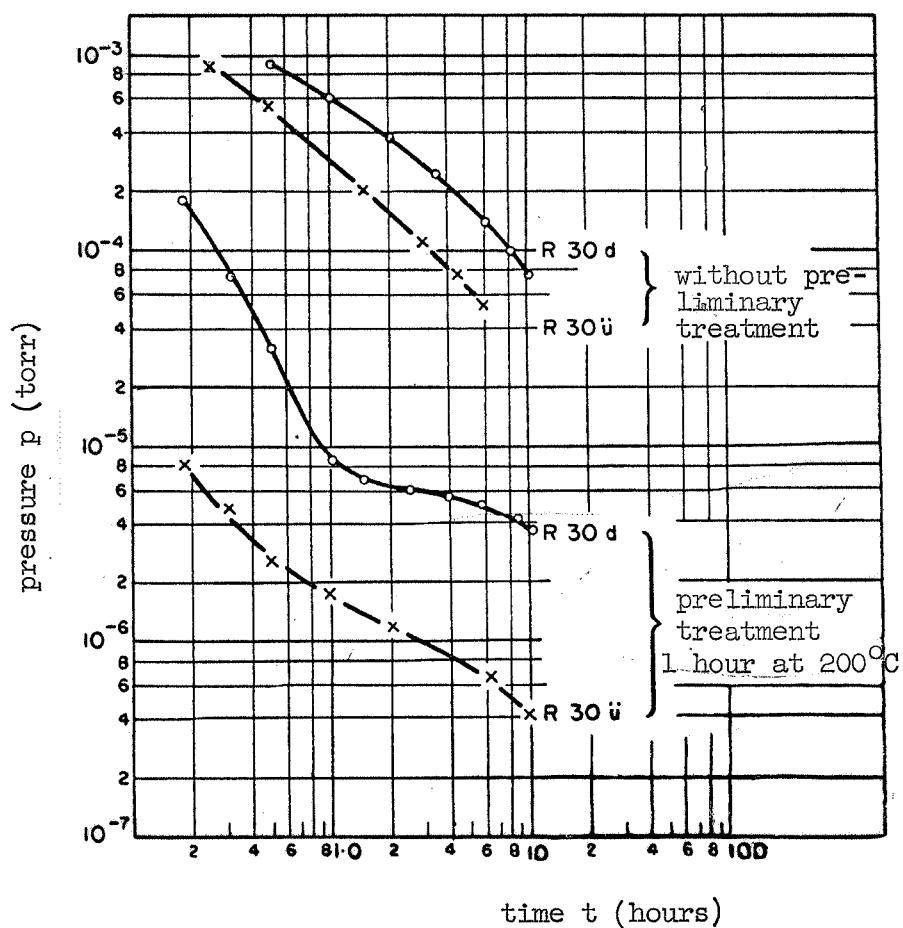


Fig. 5.

Among these elementary processes we can afford to disregard physical adsorption, since with the methods usually employed in vacuum technology such loosely bound gas molecules are generally very quickly removed into the gas space. In connection with chemisorption and the dissolution of the gas molecules in solid walls or their diffusion through such walls, particular importance attaches to the question whether for a given outgassing treatment desorption from the chemisorbed state or diffusion through the solid walls is decisive in relation to time. Certainly, desorption can be accelerated by raising the temperature, but if this results in the diffusion being so intensified that

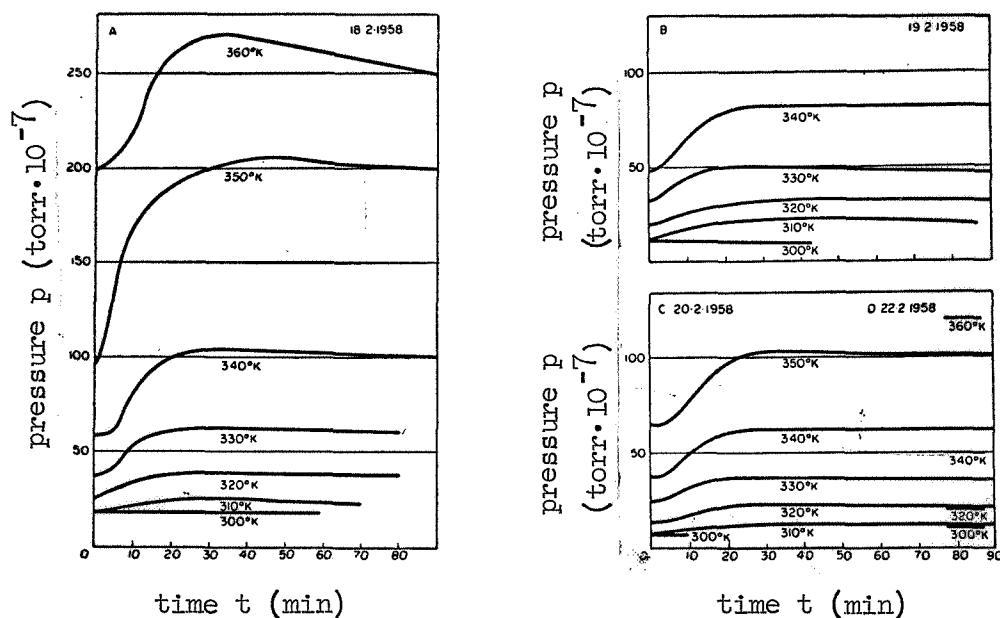


Fig. 6. Gas evolution at different temperatures (Araldit). In each case the pressure-time curves were measured immediately after the temperature of the vessel was raised to the value given as parameter. For each curve the zero point on the time scale coincides with the moment the vessel temperature was raised (after Schittko).

additional supplies from the atmosphere are furnished more rapidly through the vessel wall, the effect of raising the temperature will actually be the opposite of that aimed at. Thus, it is of the utmost

importance to know how the outgassing process is affected at different temperatures by desorption or diffusion through the solid wall. This problem has been tackled from various angles, notably by Kraus [11] (see Fig. 4), but Schram's discussion [16] is particularly thorough. If the evolution of gas from the surface (q) expressed as a function of time is expanded in powers of t , and only the first term of the series is considered, it is possible to draw conclusions concerning the dominant process in relation to time. If q depends on the time as $1:\sqrt{t}$, we may conclude that the dominant process is diffusion; a dependence of $1:t$, on the other hand, would point to desorption as the dominant influence. In certain circumstances it would also be necessary to consider the effect of dissociation, as illustrated by Fig. 4 (based on Schram's work [16]). Of course, the results of such analyses should be treated cautiously. (1) Does the method presuppose that the higher powers of the time expansion can be neglected and (2) does the shape of the curve for dominant desorption depend on the shape of the adsorption isotherms that determine the process.

If, in connection with this analysis, we cast another glance at Fig. 2, which gives the gas evolved by different materials, we see that the curves for the metals have an essentially steeper slope than those for plastics, from which we must conclude that with metals desorption and with plastics diffusion are the time-controlling factors. I would like to postpone consideration of these problems, however, and return to them at a later point. In this connection, a certain interest attaches to Fig. 5, which shows the pressure-time curve in a measuring chamber during the outgassing of varieties of silicone rubber, based on measurements made by my colleague H. v. Münchhausen. The upper two curves for untreated silicone resemble those for plastics in Fig. 2. The lower two curves for pretreated silicone rubber are particularly interesting. These specimens were kept in a drying oven for one hour at 200°C and atmospheric pressure. Then the lower two curves were registered. It is clear that these curves can be divided into three parts. The first part, characterized by a steeper slope, would correspond to a region in which desorption is dominant; the second part, with a somewhat gentler slope, corresponds to a region in which diffusion is the controlling process; the third part, the tail of the curve, returns to the steeper slope. These results, together with those still to be reported, indicate that there is always an interplay between desorption from the surface and replenishment by diffusion from the interior of the material. In a state of stationary equilibrium, the slower process of diffusion is decisive, as far as silicone rubber is concerned. If stationary conditions are disturbed by preliminary treatment, the more rapid process of desorption also comes into prominence, until uniform distribution over the solid has been restored, whereupon the diffusion process again becomes dominant. Finally, the concentration inside the solid begins to decline, with the result that the total desorption rate must fall, which would explain the third part of the curves reproduced here.

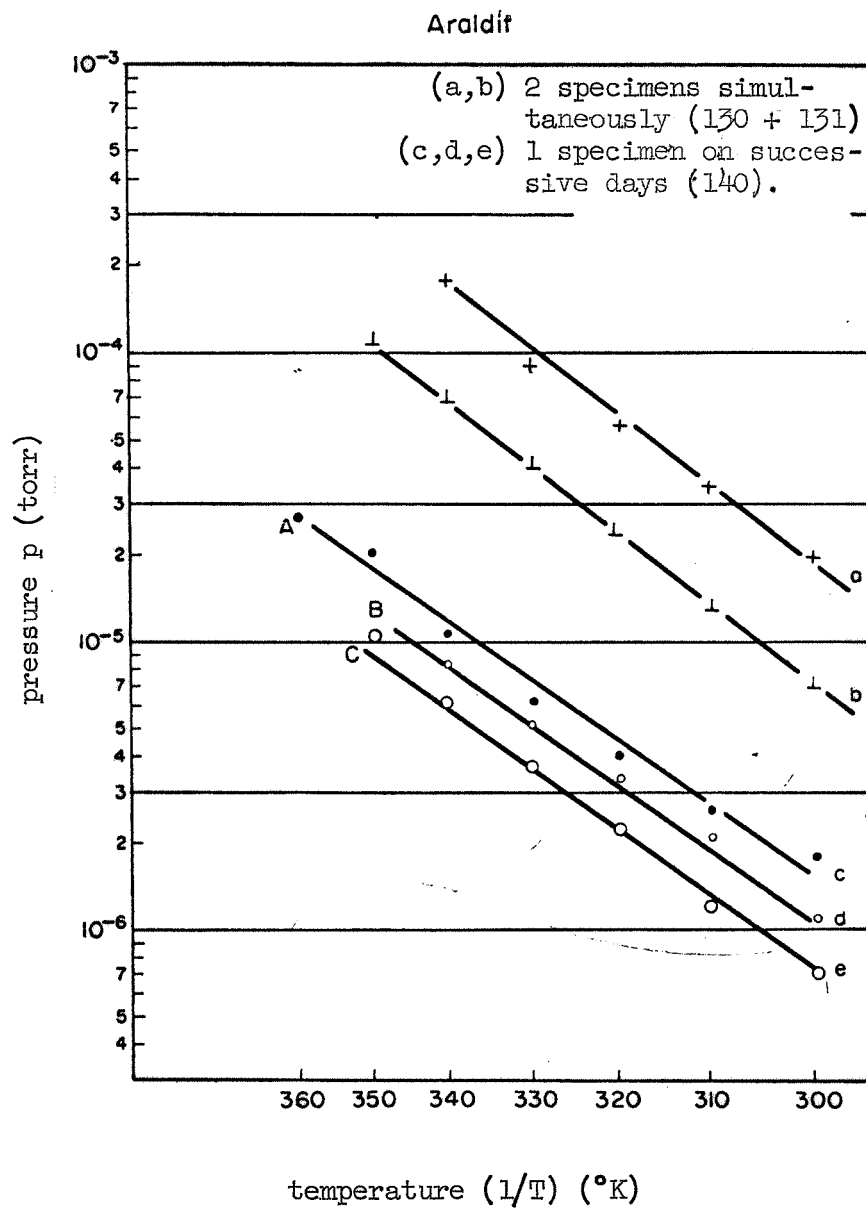


Fig. 7. Gas evolution at different temperatures (Araldit). Pressure vs. $1/T$ (after Schittko). Calculated activation energies of the order of 10 kcal/mole.

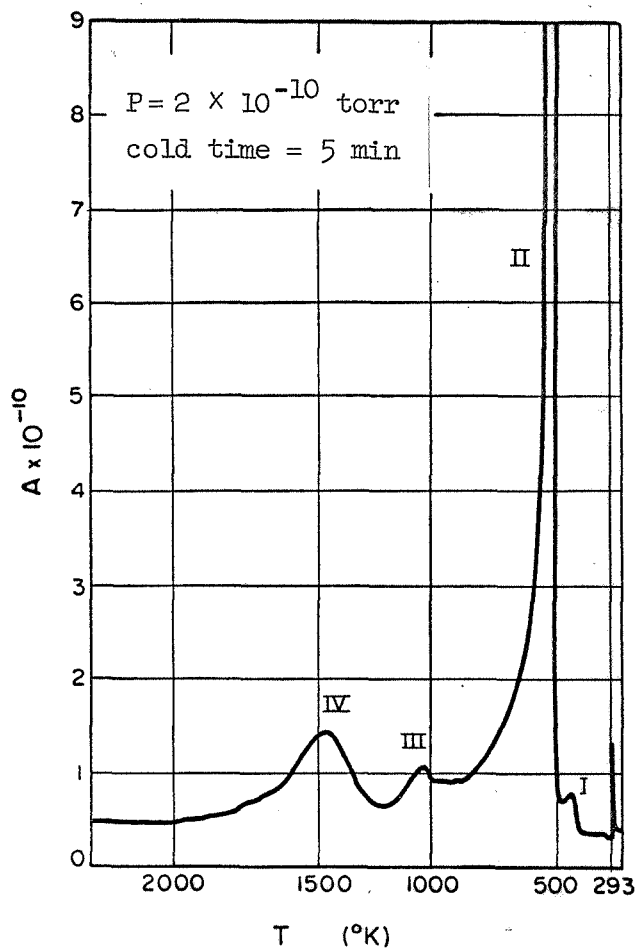


Fig. 8. Residual gas spectrum (Redhead method) for a total pressure of $2 \cdot 10^{-10}$ torr.

As an example of gas evolution measurements at increased temperatures, I offer Fig. 6, based on measurements made by my colleague Schittko on the evolution of gas from Araldit specimens when the temperature is raised stepwise. The analysis of these measurements of the gas evolution as a function of temperature, plotted as the log of the gas evolution in Maseinum against $1/T$, gives straight lines, the slope of which is a measure of the activation energy of the desorption process

(Fig. 7). The measured activation energies, obtained in this way, are of the order of 10 kcal/mole and are thus in agreement with Redhead's values for higher temperatures [13] and the data of Schram [16]. Redhead investigated the influence of temperature on the desorption process by a rather different method, involving the slow heating of gas-charged wires, and found that at special temperatures, critical for the different gases, a very strong evolution of gas was suddenly to be observed. The pressure peaks thus measured for constant increase in temperature and simultaneous pressure registration (Fig. 8) are a measure of the characteristic temperature of the desorption process and hence of the desorption energy.

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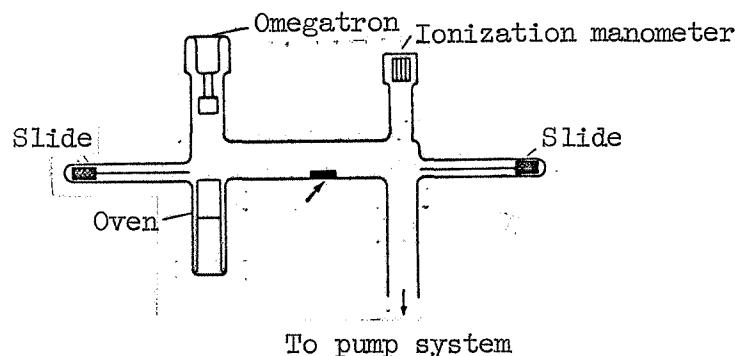


Fig. 9. Apparatus for measuring gas evolution at increased temperature (after Flecken and Nöller).

My colleagues Flecken and Nöller have also made measurements of gas evolution at higher temperatures, in particular under ultrahigh-vacuum conditions. They used an apparatus of the type illustrated in Fig. 9. I shall only dwell briefly on this work, since it is described in detail elsewhere in this symposium. The gas evolution of a specimen in an ultrahigh-vacuum system at room temperature can be measured with an omegatron and an ionization manometer and then by means of two magnetic slides the specimen can be transported to and removed from a furnace previously brought to a certain increased temperature. By way of example, Fig. 10 shows curves recorded in this way for the gas evolution into an ultrahigh vacuum as a function of the time after the introduction of the specimen into the hot furnace. The curve recorded at a temperature of 200°C shows that at this low temperature it is mainly

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water vapor that is desorbed. By contrast, the curve for 450°C indicates the presence of CO, CO₂, H₂ and various hydrocarbons, as well as water vapor.

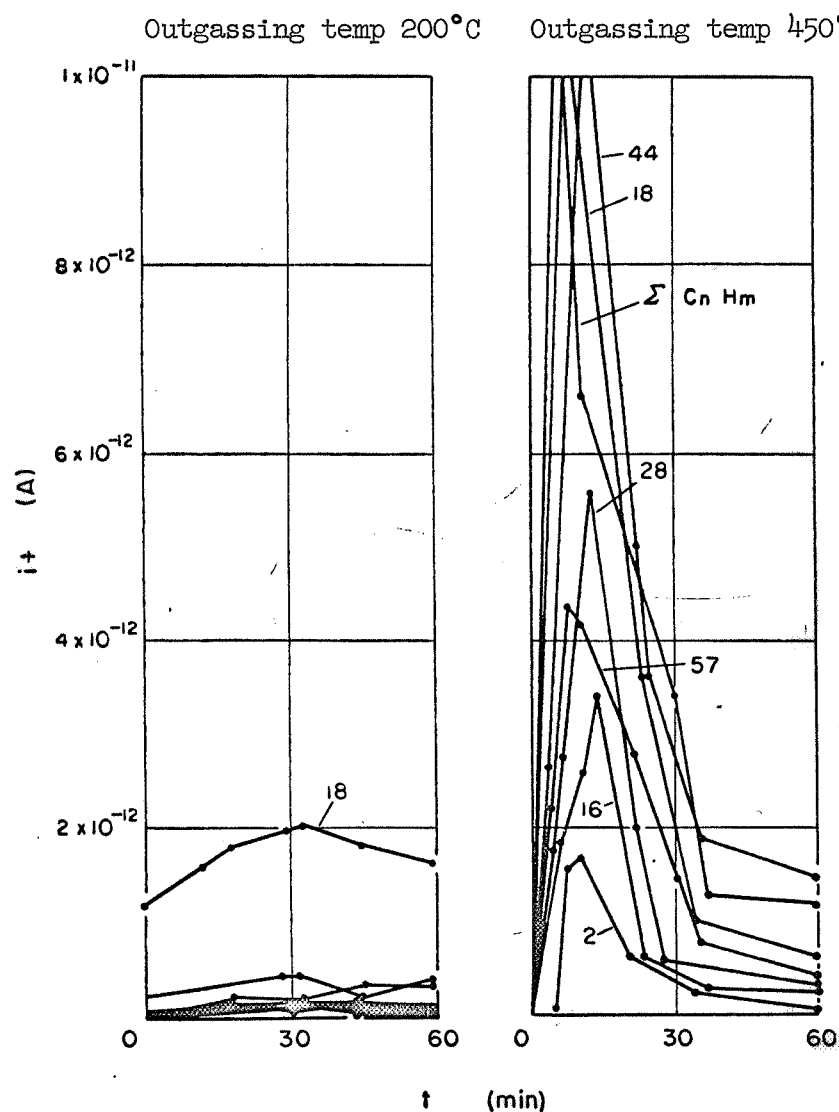


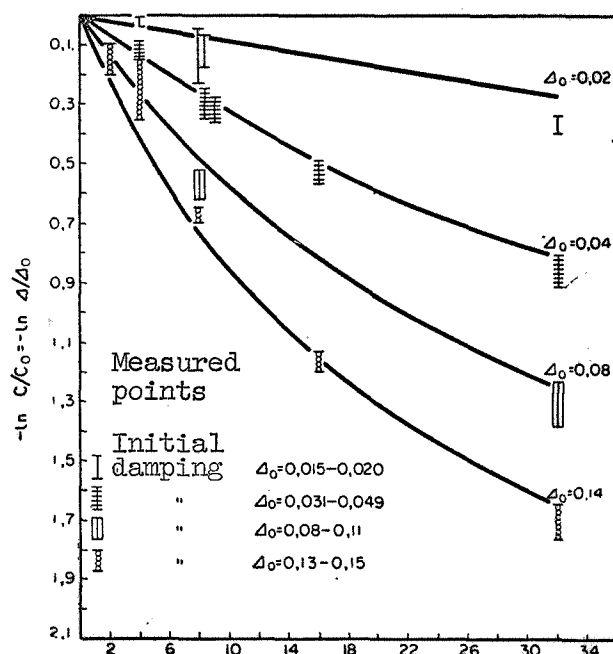
Fig. 10. Curves of differential gas evolution at different temperatures (after Flecken and Nöller). Numbers attached to curves = molecular weight of type of gas evolved.

Table 1

P = c • D

(All figures apply to room temperature)

	Gas evolution	Gas evolution after 5 hrs.	Solubility C	Diffusion Coefficient D	Permeability P	Activation energy
	$\frac{\text{torr l.}}{\text{sec cm}^2}$	$\frac{\text{torr l.}}{\text{sec cm}^2}$	$\frac{\text{cc (NTP)}}{100 \text{ g l. torr}}$	$\frac{\text{cm}^2}{\text{sec}}$	$\frac{\text{cc (NTP)}}{\text{sec cm}^2 \text{ mm torr}}$	cal/mole
Metals	10^{-7}	10^{-9}	10^{-2}	$< 10^{-9}$	$< 10^{-9}$	$> 20 \cdot 10^3$
Ceramics	10^{-6}	10^{-8}			10^{-13}	
Glass/quartz			$10^{-4}-10^{-5}$	10^{-10}	$10^{-12}-10^{-13}$	$6 \cdot 10^3$
Plastics	10^{-5}	10^{-7}	$10^{-2}-10^{-3}$	$10^{-6}-10^{-7}$	$10^{-10}-10^{-12}$	$5-10 \cdot 10^3$



Duration of outgassing process (hours)

Fig. 11. Investigations of the desorption of N_2 from α -iron at $700^\circ C$ into a high vacuum (after Junge). The four curves show that the decrease in concentration c depends on the initial concentration c_0 . Presence of a bimolecular surface reaction.

As a last method of measuring gas evolution at increased temperatures, I would like to mention a method that my colleague Junge [9] has recently used with success. It consists in applying the known method of resonance damping of elastic vibrations by means of gases dissolved in the vibrating metal. As is known, the decrement depends on the temperature and the amount of gas dissolved, to which the measured maximum amplitude of the vibration is proportional. Thus, with this method, as distinct from all the other methods so far described, the evolution of gas can be determined not only from the increase in the amount of gas in the gas space, but directly from the decrease in the amount of gas in the metal itself, which, of course, is an important new

approach. I shall merely mention briefly that in this way we have investigated the desorption of nitrogen from α -iron at temperatures of up to 700°C. Fig. 11 shows the decreases in the decrement (Δ) or concentration (C) of nitrogen dissolved in α -iron as a function of the time (t) during which the iron wire being outgassed was kept in a vacuum at 700°C. Initially, the measured values, shown together with the corresponding errors, do not appear to define a regular curve. Nevertheless, it can be seen that the outgassing process as a whole proceeds very slowly. Comparison with Fast's earlier measurements [17] on the diffusion of nitrogen in α -iron shows that the outgassing process as a whole proceeds more slowly than diffusion. Thus, the desorption process must control the outgassing time. If we further assume that the desorption process is linked with the recombination of pairs of N atoms to form N_2 molecules, the desorption will be described by a differential equation of the form:

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$$\frac{dc}{dt} = -Kc^2.$$

The curves for the solution of this differential equation depend on the initial concentration c_0 or the initial damping Δ_0 . The curves in Fig. 11 have been plotted for four initial concentrations. Clearly, the measured points can to a large extent be distributed over these four curves. This would mean that the assumption concerning the contributions of the various elementary processes to the outgassing of nitrogen in α -iron is a reasonable one. Thus, rapid diffusion from the interior of the α -iron would be followed at the surface of the iron by a slow desorption process, linked with the recombination of atomic to molecular nitrogen, that controls the course of the outgassing process.

Finally, Table I gives the physical constants that determine the outgassing processes for the following groups: metals, ceramics, glasses and quartz, and plastics. The data, of course, are only averaged, since the numerical values vary considerably within the individual groups.

DISCUSSION

D. Alpert, University of Illinois: What is the range of pressures your method can detect?

Answer: Range from 10^{-4} to 10^{-8} Torr.

A. E. Barrington, Varian: How is the attenuation of the molecular beam measured?

Answer: The molecular beam consists of neutral potassium atoms. They are detected with a Langmuir-Taylor Detector (a hot tungsten wire for the ionization of the impinging neutral atoms and a surrounding negative grid for collecting the positive ions).

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